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(54) PROCESS AND ACCELERATOR SYSTEM FOR THE VULCANISATION OF RUBBERS

(71) We, SCHILDKRÖT AG vORMALS RHEINISCHE GUMMI-UND CELLULOIDFABRIK, of 8 Gummistrasse, Mannheim-Neckarau, Germany, a Corporation organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention is concerned with a process for the vulcanisation of rubbers with a low degree of unsaturation, especially of isobutylene-isoprene co-polymers (IIR), ethylene-propylene-diene terpolymers (EPDM) or mixtures thereof.

15 Of the elastomers used in technology, the co-polymer of isobutylene and isoprene (IIR) and the terpolymer of ethylene, propylene and a diene with non-conjugated double bonds (EPDM) have a low content of reactive double bonds which are available for cross-linking.

20 IIR usually has a degree of unsaturation of between 1 and 3 mole % and, at the moment, EPDM is known with a degree of unsaturation of between 0.6 and 2.5 mole %. Styrene-butadiene rubber has, by way of comparison, a degree of unsaturation of about 80 mole %. Because of their low proportion of unsaturated bonds, the vulcanisation velocity of IIR and 25 EPDM is undesirably low, even in the case of the use of highly efficient ultra-accelerators.

30 For the vulcanisation of rubbers of this type with a low degree of unsaturation, various kinds of accelerators are known. Thus, for example, a sulphur vulcanisation is carried out with an accelerator system consisting of a thiazole derivative and a metal dithiocarbamate, optionally in combination with an accelerator of the thiuram sulphide type.

35 The so-called quinone vulcanisation makes use of a cross linker system of quinone dioxime or *p,p'*-dibenzoyl-quinone-dioxide and lead oxides, optionally with the addition of an accelerator of the thiazole type.

40 Furthermore, resin vulcanisation can also be

carried out with the use of a system comprising dimethylol-phenol resins and a halogen-containing activator.

The vulcanisation with the above-mentioned systems is, in the case of the known processes, carried out at temperatures of more than 140°C. and usually in an autoclave, in order that it may take place within an economically feasible period of time. Only the quinone vulcanisation takes place quickly enough in order, for example, to be of use in the production of cables in a continuous vulcanisation process but, nevertheless, at high temperatures.

45 It is an object of the present invention to provide a vulcanisation process and an accelerator therefor which enables rubber with a low degree of unsaturation to be vulcanised at only moderately elevated temperatures.

50 The process according to the present invention is characterised in that, in addition to sulphur, a dithiocarbamate accelerator and a thiazole accelerator, there is used a guanidine accelerator and at least one further dithiocarbamate accelerator. In this way, a vulcanisation under mild conditions of IIR or of EPDM or 55 of mixtures thereof is possible at temperatures below 100°C. within a period of 24 hours.

55 Examples of dithiocarbamates which can be used according to the present invention include zinc ethyl-phenyl dithiocarbamate, zinc di-butyl-dithiocarbamate, zinc dimethyl dithiocarbamate, zinc diethyl dithiocarbamate, copper dimethyl dithiocarbamate, cadmium diethyl dithiocarbamate, tellurium diethyl dithiocarbamate, sodium cyclohexyl-ethyl-dithiocarbamate, zinc N - pentamethylene - dithiocarbamate, lead dimethyl dithiocarbamate and N-pentamethylene - ammonium - pentamethylene-dithiocarbamate.

60 Examples of guanidines which can be used according to the present invention, include diphenyl-guanidine, *o*-tolyl-biguanide and *o*-tolyl-guanidine.

65 Examples of thiazoles which can be used according to the present invention include 2-

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mercapto-benzothiazole, benzothiazyl disulphide, dibenzo-thiazyl disulphide and the reaction products thereof.

It is especially advantageous to use those dithiocarbamate accelerators which differ by the organic radical attached to the nitrogen atom and/or by the metal, ammonium or organo-ammonium ions.

Thus, for example, the use of a vulcanisation accelerator consisting of zinc ethyl-phenyl-dithiocarbamate, zinc dibutyl-dithiocarbamate, diphenyl-guanidine and 2- mercaptobenzothiazole in the presence of sulphur, leads, within a period of 24 hours at only 80°C., even in the case of a butyl rubber with a degree of unsaturation of only 1 mole %, to complete vulcanisation. The vulcanisation or scorch time can be regulated by variation of the amount ratio of the accelerator in such a range that an admixture of the whole vulcanisation system is possible in an intimate mixer, such as a plunger kneader or a Banbury mixer.

An especial advantage of the vulcanisation according to the present invention at temperatures below 100°C. is that it is not necessary to use hot steam, pressure resistant vulcanisation vessels are not necessary and, even in the case of the use of thick layers of material there is obtained a uniform and extraordinarily gently vulcanised article which is substantially stress-free. On the other hand, it is also possible to vulcanise, with the above-described vulcanisation system, for example, profiled articles in a salt bath (LCM process), since the vulcanisation velocity in the process according to the present invention is very rapid at high temperatures. The vulcanisation is preferably carried out in hot air.

It is especially advantageous to use 0.5—4.0 parts by weight of dithiocarbamate, 0.1—1.0 parts by weight of a thiazole, 0.1—1.0 parts by weight of a guanidine and 0.5—2.0 parts

by weight of sulphur per 100 parts by weight of rubber.

The vulcanisation is preferably carried out at temperatures of 70—120°C., especially of 75—90°C.

In known manner, there can be added to the rubber one or more additives selected from strengthening filler materials, plasticisers, extender oils, light protection agents and anti-ageing agents.

The combination of the vulcanisation accelerators for the carrying out of the process according to the present invention contains at least two different dithiocarbamates, a thiazole and a guanidine.

It preferably contains metal and/or ammonium salts of N-disubstituted dithiocarbamates, the substituents being alkyl, alkylene, cycloalkyl and/or aryl radicals. In particular, there can be used the above-mentioned dithiocarbamates, guanidines and thiazoles.

The following Examples are given for the purpose of illustrating the present invention, the figures given in the formulations being parts by weight:—

EXAMPLE 1.

Basic formulation:

IIR (1 mole % unsaturation)	100.0	70
FEF-carbon black	50.0	
HAF-carbon black	35.0	
SRF-carbon black	30.0	
zinc oxide, active	5.0	
light protection wax	3.0	75
stearic acid	1.0	
N-phenyl-N'-isopropyl-p-phenylene-diamine	1.0	
extender oil	10.0	
polyethylene wax	8.0	80

The results obtained for the vulcanisation of this formulation with various accelerator systems, are set out in the following Table:

Accelerator system	A	B	C	D	E	F
Zinc Ethyl-phenyl dithiocarbamate	0.7	0.7	0.7	0.7	—	—
Zinc dibutyl dithiocarbamate	3.0	3.0	3.0	3.0	1.5	1.5
N-Pentamethyleneammonium-pentamethylene dithiocarbamate	—	—	—	1.5	—	—
2-Mercaptobenzothiazole	0.5	0.5	0.5	0.5	1.0	1.5
Dibenzothiazyl disulphide	—	—	—	—	0.5	—
Diphenyl guanidine	1.2	0.5	—	0.3	—	0.5
Sulphur	1.2	1.2	1.2	1.5	1.2	1.2
Mooney t_6	4'30"	6'00"	9'00"	5'00"	8'45"	12'30"
Mooney t_{35}	7'40"	10'30"	18'35"	8'45"	34'15"	26'00"
Vulcanisation temperature (°C)	80	80	80	80	80	160
Vulcanisation time (hr.)	24	24	36	16	72	0.33
Shore A	69	68	62	69	65	70
Tensile strength (kp/cm ²)	82	80	62	86	81	86
Total extension (%)	525	650	600	670	725	650
Tension value at 300% elongation (kp/cm ²)	60	40	40	45	27	56

Example 1 shews that the vulcanisation velocity can be varied within wide limits by appropriate variation of the vulcanisation system. If one component is missing, such as the guanidine in Example 1C, or if only one dithiocarbamate is used, as in Examples 1E and 1F, then, with the use of the same temperature, the vulcanisation times are prolonged considerably or high vulcanisation temperatures are necessary or, at temperatures below 100°C., no vulcanisation at all is obtained, as in Example 1F, where, after 96 hours at 80°C., a tensile strength of only 14.6 kp/cm² is obtained, which corresponds to the green strength of the mixture.

EXAMPLE 2.

This Example shews the comparison of a conventional mixture of accelerators (2A) with

a mixture of accelerators according to the present invention (2C). Example 2B shews a compromise between the two vulcanisation systems which, in spite of relatively favourable Mooney values, gives a product with unsatisfactory mechanical values.

<i>Basic formulation:</i>	25
IIR (1 mole % unsaturation)	100.0
SRF-carbon black	30.0
FEF-carbon black	30.0
HAF-carbon black	20.0
kaolin	50.0
zinc oxide, active	5.0
light protection wax	3.0
N-phenyl-N'-isopropyl-p-phenylene-diamine	1.0
extender oil	10.0
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Accelerator system	A	B	C
Tetramethylenethiuram disulphide	1.0	—	—
2-Mercaptobenzothiazole	0.5	—	0.5
Zinc diethyl dithiocarbamate	0.3	—	—
Zinc ethyl-phenyl dithiocarbamate	—	0.7	0.7
Zinc dibutyl dithiocarbamate	—	3.0	3.0
Diphenyl-guanidine	—	0.5	0.5
Sulphur	1.5	1.2	1.2
Mooney t_5 (min.)	12'30"	7'10"	8'45"
Mooney t_{35} (min.)	21'00"	16'45"	14'00"
Vulcanisation temperature (°C.)	145	80	80
Vulcanisation time (hr.)	1	36	24
Shore A	64	53	63
Tensile strength (kp/cm ²)	82	37	74
Total extension (%)	520	440	550
Tension value at 300% elongation (kp/cm ²)	49	25	28

EXAMPLE 3.

In this Example, there is compared a conventional acceleration of EPDM (the diene of which is ethylidenenorbornene in Example 3A and dicyclopentadiene in Example 3B) with tetramethylthiuram disulphide, zinc diethyl thiocarbamate, 2-mercaptopbenzothiazole and sulphur with the vulcanisation process according to the present invention. The conventional acceleration gives an optimum vulcanisation at 160°C. after 20 minutes. When an attempt is made to carry out the vulcanisation at 80°C. without pressure and in hot air then, even after 96 hours, optimum vulcanisation properties are still not reached. It is also a disadvantage of the known process that the system used in Examples 3A and 3B still shew a strong sulphur bloom after 24 hours.

Examples 3C—3F, in which there is used EPDM rubber Cetan 720, shew that, by variation of the proportions of the components of the system according to the present invention, the vulcanisation times can be correspondingly varied. If one component is absent, such as the diphenyl-guanidine in Example 3G, then the vulcanisation time increases to the value of the conventional system.

Basic formulation:

EPDM (0.7 mole % unsaturation)	100.0	
Zinc oxide	5.0	30
stearic acid	1.0	
FEF-carbon black	45.0	
SRF-carbon black	45.0	
naphthenic processing oil	50.0	

Vulcanisation system	A	B	C	D	E	F	G
Tetramethylene-thiuram disulphide	1.0	1.0	—	—	—	—	—
2-Mercaptobenzothiazole	0.5	0.5	0.5	0.5	0.4	0.5	0.5
Zinc diethyl dithiocarbamate	1.5	1.5	—	—	—	—	—
Zinc dibutyl dithiocarbamate	—	—	3.0	3.0	3.0	3.0	3.0
Zinc ethyl-phenyl dithiocarbamate	—	—	0.7	0.7	0.7	0.7	0.3
N-Pentamethylene ammonium-pentamethylene dithiocarbamate	—	—	1.0	—	—	—	—
Diphenyl-guanidine	—	—	0.5	0.5	0.5	1.2	—
Zinc-N-pentamethylene dithiocarbamate	—	—	—	1.0	—	—	—
Sulphur	1.5	1.5	1.2	1.2	1.2	1.2	1.2
Mooney t_5	22'00"	22'00"	6'20"	7'30"	8'00"	8'15"	15'00"
Mooney t_{35}	35'45"	35'45"	13'35"	11'30"	14'30"	20'30"	37'00"
Vulcanisation temperature (°C.)	160	80	80	80	80	80	80
Vulcanisation time (hr.)	0.33	96	36	16	24	48	96
Shore A	61	54	59	61	61	59	56
Tensile strength (kp/cm ²)	118	90	95	120	118	107	81
Total extension (%)	380	415	550	650	400	520	540
Tension value at 300% elongation (kp/cm ²)	83	70	66	65	60	71	57

WHAT WE CLAIM IS:—

1. An accelerator system for carrying out the vulcanisation of rubbers with a low degree of unsaturation, said system comprising at least two different dithiocarbamates, a thiazole and a guanidine.
2. A system according to claim 1, wherein the dithiocarbamates are metal and/or ammonium and/or organo-ammonium salts of N-disubstituted dithiocarbamates, the substituents being alkyl, alkylene, cycloalkyl and/or aryl radicals.
3. A system according to claim 2, wherein the dithiocarbamates are selected from zinc ethyl-phenyl-dithiocarbamate, zinc dibutyl-dithiocarbamate, zinc dimethyl-dithiocarbamate, zinc diethyl-dithiocarbamate, copper dimethyl-dithiocarbamate, cadmium diethyl dithiocarbamate, tellurium diethyl-dithiocarbamate, sodium cyclohexyl-ethyl-dithiocarbamate, zinc N-pentamethylene-dithiocarbamate, lead dimethyl-dithiocarbamate and N-pentamethylene - ammonium pentamethylene - dithiocarbamate.
4. A system according to any of the preceding claims, wherein the guanidine is diphenyl-guanidine, *o*-tolyl-biguanide or di-*o*-tolyl-guanidine.
5. A system according to any of the preceding claims, wherein the thiazole is 2-mercaptopbenzothiazole, benzothiazyl disulphide or dibenzothiazyl disulphide.
6. A system according to any of claims 2—5, wherein the dithiocarbamates used differ from one another in the nature of the organic radicals on the nitrogen and/or by the metal, ammonium or organo-ammonium ions.
7. A system according to any of the preceding claims, containing 0.5—4.0 parts by weight of the dithiocarbamates, 0.1—1.0 parts by weight of the thiazole and 0.1—1.0 parts by weight of the guanidine.
8. An accelerator system according to claim 1 for carrying out the vulcanisation of rubbers with a low degree of unsaturation, substantially as hereinbefore described and exemplified.
9. Process for the vulcanisation of rubbers with a low degree of unsaturation, wherein there is used sulphur and an accelerator system according to any of claims 1—8.
10. Process according to claim 9, wherein there are used 0.5—4.0 parts by weight of the dithiocarbamates, 0.1—1.0 parts by weight of the thiazole, 0.1—1.0 parts by weight of the guanidine and 0.5—2.0 parts by weight of sulphur per 100 parts by weight of rubber.
11. Process according to claim 9 or 10, wherein the vulcanisation is carried out at a temperature of 70—120°C.
12. Process according to claim 11, wherein the vulcanisation is carried out at a temperature of 75—90°C.
13. Process according to any of claims 9—12, wherein the vulcanisation is carried out in a salt bath.
14. Process according to any of claims 9—12, wherein the vulcanisation is carried out in hot air.
15. Process according to any of claims 9—14, wherein the vulcanisation is carried out with the use of one or more additives selected from strengthening filler materials, plasticisers, extender oils, light protection agents and anti-ageing agents.
16. Process according to any of claims 9—15, whenever applied to co-polymers of isoprene and isobutylene or to terpolymers of ethylene, propylene and a diene.
17. Process according to claim 9 for the vulcanisation of rubbers with a low degree of unsaturation, substantially as hereinbefore described and exemplified.
18. Rubbers with a low degree of unsaturation, whenever vulcanised by the process according to any of claims 9—17.

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